



# Revealing the promotion/inhibition mechanism of $\text{CO}_3^{2-}$ in the oriented electrocatalytic conversion of ethane to 2-propanol and acetone

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## ARTICLE INFO

### Keywords:

Electrochemical ethane oxidation  
Ethane conversion in room temperature  
Ethane converted to 2-propanol  
Side reaction competition  
 $\text{CO}_3^{2-}$  adsorption mechanism on lattice O/O defects

## ABSTRACT

Ethane conversion is an important industrial process, however, the conversion of ethane into high value-added chemicals at room temperature has rarely been studied. Herein, a  $\text{NaCo}_2\text{O}_4/\text{CeO}_2$  has been fabricated to convert ethane to 2-propanol and acetone, in which Na was introduced in  $\text{Co}_3\text{O}_4$  to change the coordination environment of Co and produce more lattice O on  $\text{NaCo}_2\text{O}_4$ . The highest selectivity of acetone could reach to 89 %. In the reaction process, the promotion effect of  $\text{CO}_3^{2-}$  and the competition between  $\text{CO}_3^{2-}$  OR and  $\text{C}_2\text{H}_6$  OR was also confirmed. After changing  $\text{Co}_3\text{O}_4$  to  $\text{NaCo}_2\text{O}_4$ , the lattice O increased and acted as active site of  $\text{C}_2\text{H}_6$  oxidation reaction. Furthermore, the defects on  $\text{CeO}_2$  made primary effects on  $\text{CO}_3^{2-}$  oxidation reaction. By combining the ATR-FTIR spectra and DFT calculation, the two pathways of  $\text{CO}_3^{2-}$  adsorption was simulated to infer the mechanism of reaction promoting process.

## 1. Introduction

As the second most abundant gas in natural gas, it is easy to cause resource waste if ethane is converted to  $\text{CO}_2$  directly. Besides, excessive emissions of  $\text{CO}_2$  can also cause greenhouse effects and lead to global warming [1]. Therefore, it is considered to convert alkane to other high-valued chemical products for meeting the demand of storage and application. Dogu and his coworkers doped La and Cl into  $\text{SrTiO}_3$  to make  $\text{La}_{0.2}\text{Sr}_{0.8}\text{TiO}_{3\pm\delta}\text{Cl}_\delta$  for converting ethane to ethylene by electrocatalysis [2]. Zhang and his team used  $\text{BaCe}_{0.7}\text{Zr}_{0.1}\text{Y}_{0.1}\text{Yb}_{0.1}\text{O}_{3-\delta}$  to electrochemical dehydrogenation of ethane to ethylene in a solid oxide electrolyzer. Furthermore, the  $\text{H}^+$  generated from ethane was also transported to cathode and combined with  $\text{CO}_2$ . In this way, the  $\text{CO}_2$  could also be reduced to CO [3]. Although ethane conversion involves the dehydrogenation of ethane to ethylene at high temperatures traditionally [4], the storage and transportation of gas product  $\text{C}_2\text{H}_4$  is still a problem that needs to be solved. In this case, electrocatalytic conversion at room temperature is needed to meet the demands of resources reasonable utilization.

Transition metal oxides are always used as an active phase in electrochemical conversion process. Jong and coworkers provided an accessible pathway for methane diffusion on the catalyst by modifying  $\text{Co}_3\text{O}_4$  onto  $\text{ZrO}_2$ , thereby reducing the onset potential of methane oxidation to convert methane to ethanol [5]. Except for  $\text{Co}_3\text{O}_4$ ,  $\text{ZrO}_2$  was

also anchored on the strong active catalyst  $\text{Cu}_2\text{O}$  (111),  $\text{ZrO}_2$  promote charge redistribution and create a quick electron transfer network to support a higher methane conversion capability [6]. In addition to consider suitable catalysts, electrocatalytic conversion of methane also requires selecting appropriate electrolytes to promote the chemical reaction and practical applications. Introducing free radicals into the reaction system can promote the smooth progress of the reaction. A molecular catalyst of vanadium (V)-oxo dimer was used to convert methane in 98 %  $\text{H}_2\text{SO}_4$ , which yields cation radicals on the sulfonic ligand that selectively activate  $\text{CH}_4$  [7]. Furthermore,  $\text{NiO}/\text{ZnO}$  shell/core nanorod catalyst in 0.5 mol/L  $\text{Na}_2\text{CO}_3$  solution can convert  $\text{CH}_4$  to ethanol [8]. More importantly, this study proved that the O in  $\text{CO}_3^{2-}$  finally became the O in ethanol by using  $\text{C}^{16}\text{O}_3^{2-}$  and  $\text{C}^{18}\text{O}_3^{2-}$ . In addition, Jaehyun Lee and coworkers analyzed the mechanism that the O in  $\text{CO}_3^{2-}$  became the OH in ethanol by DFT calculation [9]. Therefore, the competition between target reactant and side reactions should also be discussed in the electrochemical reaction process.

In this case, it is important to design reasonable electrocatalysts since side reactions in electrochemical reaction process is the key factor to determine the catalysts performance. Li and coworkers manufactured iron-nickel hydroxide ( $\text{Fe-Ni-OH}$ ) nanosheet to convert  $\text{CH}_4$  in 0.1 mol/L NaOH, which was found to produce  $\text{Ni}^{\text{III}}\text{OOH}$  to serve as active sites in reaction process [10]. Besides, the competition between OER and  $\text{CH}_4$  oxidation reaction was also found, leading to choose the most active and

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<https://doi.org/10.1016/j.apcatb.2024.124063>

Received 26 January 2024; Received in revised form 23 March 2024; Accepted 8 April 2024

Available online 9 April 2024

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selectivity catalysis among all samples. To control the competition between OER and ethanol oxidation reaction (EOR), Wang and his team use Chemisorbed octadecylamine ligands to create a layer at the ultrathin  $\text{Ni}(\text{OH})_2$  nanosheets surface to improve EOR activity and selectivity by promoting alcohol diffusion and adsorption in an alkaline solution [11]. Furthermore, Geng and his coworkers manufactured a immobilized Ag pyrazole (AgPz) molecular catalyst to control the strong  $^*\text{OH}$  binding energy to promote the  $\text{H}_2\text{O}$  dissociate into  $^*\text{OH}$ , then the AgPz reversibly changed to AgPz-Hvac with a weak  $^*\text{OH}$  binding energy, which promote the Propylene convert to Propylene Glycol [12]. The reversible changing process is the main reason to avoid the strong  $^*\text{OH}$  binding energy hinder the propylene oxidation reaction.

In this study, Na atoms were doped in the spinel type metal oxide  $\text{Co}_3\text{O}_4$  to change the chemical valence state and coordination environment of Co in order to obtain a higher ethane oxidation performance. To adjust the performance of the  $\text{CO}_3^{2-}$  oxidation reaction, the content of  $\text{CeO}_2$  was changed in  $\text{NaCo}_2\text{O}_4/\text{CeO}_2$  by adding different qualities of  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ . To explore the  $\text{Co}_3\text{O}_4$  being changed by Na during the preparing process, TG and XRD was used to detect the intermediate products in different calcination temperature. By comparing the  $\text{CO}_3^{2-}$  oxidation reaction ( $\text{CO}_3^{2-}$  OR) and  $\text{C}_2\text{H}_6$  oxidation reaction ( $\text{C}_2\text{H}_6$  OR) performance of catalysts and combining the XPS results, the active site of  $\text{C}_2\text{H}_6\text{OR}$  was confirmed as the lattice O on  $\text{NaCo}_2\text{O}_4$  and the  $\text{CO}_3^{2-}$  OR mainly occurred on the defects of catalysts. Besides, after confirming the best potential and the most suitable  $\text{Na}_2\text{CO}_3$  solution concentration by detecting products after 6 h, the pathway of ethane conversion to 2-propanol was inferred by testing in situ attenuated total reflectance Fourier transform infrared (ATR-FTIR) experiments. Finally, DFT calculation was used to confirm the competition between  $\text{C}_2\text{H}_6$  OR and  $\text{CO}_3^{2-}$  OR and detect the possible mechanism of  $\text{CO}_3^{2-}$  OR promotion process.

## 2. Experimental

### 2.1. Preparation of two-phase composite catalysts $x\text{NaCo}_2\text{O}_4/\text{CeO}_2$

Using solution combustion method to produce  $x\text{NaCo}_2\text{O}_4/\text{CeO}_2$ . To produce  $\text{NaCo}_2\text{O}_4/\text{CeO}_2$ , dissolve the metal precursors  $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  (0.868 g) and  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (0.582 g) with the molar ratio of Co:Ce=1:1 in DI water, the molar ratio of Co:Ce=2:1 and 4:1 were also calculated to produce  $2\text{NaCo}_2\text{O}_4/\text{CeO}_2$  and  $4\text{NaCo}_2\text{O}_4/\text{CeO}_2$  using the same method mentioned next. Under continuous stirring, dissolve EDTA-2Na (1.5 g) and citric acid (1.5 g) in the above mixture in turn (The Na: Co: Ce=4.4:1:1 in  $\text{NaCo}_2\text{O}_4/\text{CeO}_2$ , the quantity of EDTA-2Na was fixed). After stirring for 20 min, adjust the pH to 8 with ammonia water ( $\text{NH}_3 \cdot \text{H}_2\text{O}$ ). Then, stir the mixture at  $80^\circ\text{C}$  to obtain a purple solution, roast to  $280^\circ\text{C}$  for 1 h. Remove and grind after cooling down, annealed to  $800^\circ\text{C}$  for 2 h. In addition, pure  $\text{NaCo}_2\text{O}_4$  and  $\text{CeO}_2$  was also synthesized in same method for comparison. The EDTA-2Na was replaced to EDTA to produce  $\text{Co}_3\text{O}_4/\text{CeO}_2$  with the same process above.

### 2.2. Electrocatalytic performance measurements

The electrocatalytic performance of  $x\text{NaCo}_2\text{O}_4/\text{CeO}_2$  was tested by linear sweep voltammetry (LSV) and electrochemical impedance spectroscopy (EIS) measurements in a three-electrode system using electrochemical workstation (DH 7003). The glassy carbon electrode ( $0.07\text{ cm}^2$ ) was used as the working electrode (WE), Pt foil as the counter electrode (CE), Ag/AgCl electrode as the reference electrode (RE). All electrocatalytic performance was tested in  $0.5\text{ mol/L Na}_2\text{CO}_3$  solution.

Mix 2 mg of catalyst with 0.68 mL of water, 0.3 mL ethanol and  $0.02\text{ mL } 5\% \text{ Nafion}$  solution, ultrasonic vibration for 20 min, and then drop  $16\text{ }\mu\text{L}$  onto the surface of the working electrode. Before testing LSV, Ar was purged for 15 min to eliminate other gases in the system, After LSV was tested,  $\text{C}_2\text{H}_6$  was also purged for 20 min to create a saturated reactants condition. Then EIS was tested in  $1.7\text{ V(vs.RHE)}$  which is the

onset potential of  $\text{CO}_3^{2-}$  OR for these catalysts, and the range of frequency was from  $100,000\text{ Hz}$  to  $0.1\text{ Hz}$  with a voltage amplitude of  $5\text{ mV}$ .

The electrochemical ethane conversion was tested by Chronoamperometry (CA) in a three-electrode system. The Pt foil and Ag/AgCl electrode were used as the counter electrode and reference electrode, respectively. The working electrode was made by carbon cloth for  $1 \times 1.5\text{ cm}$  and make sure that  $1\text{ cm}^2$  carbon cloth was in solution. To make ink solution, 8 mg catalyst was dispersed in a mixed solution including  $1.5\text{ mL}$  water and  $1.5\text{ mL}$  ethanol by ultrasonic machine for 20 min. Add  $30\text{ }\mu\text{L } 5\% \text{ Nafion}$  solution on carbon cloth after it was washed by water and dried on  $40^\circ\text{C}$ . After assembling the three electrodes, add  $23\text{ mL Na}_2\text{CO}_3$  solution on electrolytic cell. LSV was tested in Ar and  $\text{C}_2\text{H}_6$ -saturated solution by bubbling for 15 min. The potential was from  $0.9$  to  $2.3\text{ V(vs.RHE)}$  and scan rate was  $5\text{ mV/s}$ . Finally, CA was used to convert ethane for 6 h by continuous blowing  $\text{C}_2\text{H}_6$ .

Tafel slope was calculated by formula below, the data was obtained from the results of current density and potential in LSV curves.

$$\eta = a + b \cdot \lg |i|$$

In this formula,  $\eta$  is the potential and we chose  $2.0\text{--}2.4\text{ V(vs.RHE)}$  as the range of calculation, as the products was occurred in  $2.1\text{ V(vs.RHE)}$ . The  $i$  is the current density.  $a$  is the constant and we use segmented fitting to obtain the slope as the  $b$  in formula.

### 2.3. Physical characterization and instruments

The X-ray diffraction (XRD) characterization of the materials was performed on a D/Max-2500 (Rigaku Corporation, Japan) using  $\text{Cu K}\alpha$  radiation ( $\lambda = 0.15406\text{ nm}$ ,  $40\text{ kV}$  and  $150\text{ mA}$ ) with a scanning range of  $10^\circ\text{--}80^\circ$  and a scanning speed of  $10^\circ/\text{min}$ . High-resolution TEM (JEOL 2010 F and FEI Talos F200S) was used to analyse the structure and element distribution for these catalysts. The XPS (Thermo Scientific Nexsa) was used to detect the chemical valence state of all catalysts. The values of binding energies were calibrated with the  $\text{C } 1\text{ s}$  peak of contaminant carbon at  $284.80\text{ eV}$ . Thermogravimetric analysis (TGA) was used to detect the changing temperature of catalysts with the heating ratio of  $5^\circ\text{C/min}$ . EPR for O defects detection was on the Bruker A300, the condition was: central magnetic field  $3500.00\text{ G}$ ; The sweeping width was  $150.00\text{ G}$ ; The sweeping time was  $30.00\text{ seconds}$ ; The microwave power was  $3.99\text{ mW}$ ; The modulation amplitude was  $1.000\text{ G}$ ; The conversion time was  $40.0\text{ ms}$ ,  $9.854854\text{ GHz}$ .

### 2.4. Product analysis

To investigate products after ethane conversion, Gas chromatography (GC 7820 A, Agilent Technologies, USA) with a flame ionization detector (FID) and a HT-PPFA column was used for product qualitative and quantitative analysis. The injection temperature was set to  $300^\circ\text{C}$ . For the FID, a flow of  $400\text{ mL/min}$  synthetic air,  $40\text{ mL/min}$   $\text{H}_2$  fuel, and  $20\text{ mL/min}$   $\text{N}_2$  make-up was applied. To identify the product, possible organic matter 2-propanol, 1-propanol, ethanol, methanol and acetone were also mixed with  $\text{Na}_2\text{CO}_3$  solution and tested by GC, respectively. After that,  $0.15\text{ mL}$  sample was mixed with  $0.25\text{ mL D}_2\text{O}$  and recorded by  $^1\text{H NMR}$  (Bruker AVANCE NEO 500 M) for qualitative analysis. The out gas was tested by Gas chromatography (GC 7920, Beijing Aulight Co. Ltd), which is equipped with FID and SE-54 column ( $50\text{ m} \times 0.32\text{ mm} \times 0.5\text{ }\mu\text{m}$ ). The injection temperature was set to  $150^\circ\text{C}$ . The temperature of column box was  $70^\circ\text{C}$ .

### 2.5. In situ ATR-FTIR experiments

To detect the intermediate products during the reaction process, in situ attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy (Nicolet iS50, Thermo Fisher, USA). The H-type interchangeable membrane Raman in-situ electrochemical cell was used

where applying the catalyst onto the silicon wafer as the working electrode, Ag/AgCl electrode as reference electrode. The Pt foil was in another side of the cell and act as counter electrode.

## 2.6. In situ EPR experiments

The  $2\text{NaCo}_2\text{O}_4/\text{CeO}_2$  catalyst was used as the working electrode (WE), Pt foil as the counter electrode (CE), Ag/AgCl electrode as the reference electrode (RE). After introducing ethane gas into the solution for 15 min, conducting conversion experiments in 2.3 V (vs.RHE) under the condition of continuous low flow rate introduction of ethane. 5,5-dimethyl-1-pyrroline N-oxide (DMPO) was used as a spin-trapping reagent for conducting EPR experiments. In situ EPR for detection was on the Bruker A300, the condition was: central magnetic field 3500.00 G; The sweeping width was 150.00 G; The sweeping time was 30.00 seconds; The microwave power was 3.99 mW; The modulation amplitude was 1.000 G; The conversion time was 40.0 ms, 9.854854 GHz.

## 2.7. Computational details

All the calculations are performed in the framework of the density functional theory with the projector augmented plane-wave method, as implemented in the Vienna ab initio simulation package [13]. The generalized gradient approximation proposed by Perdew, Burke, and Ernzerhof is selected for the exchange-correlation potential [14]. The cut-off energy for plane wave is set to 400 eV. The energy criterion is set to 10–5 eV in iterative solution of the Kohn-Sham equation. All the structures are relaxed until the residual forces on the atoms have

declined to less than 0.05 eV/Å.

To obtain the adsorption performance of different reactants at various interface sites, the adsorption energy ( $E_{\text{ads}}$ ) is calculated as follows:

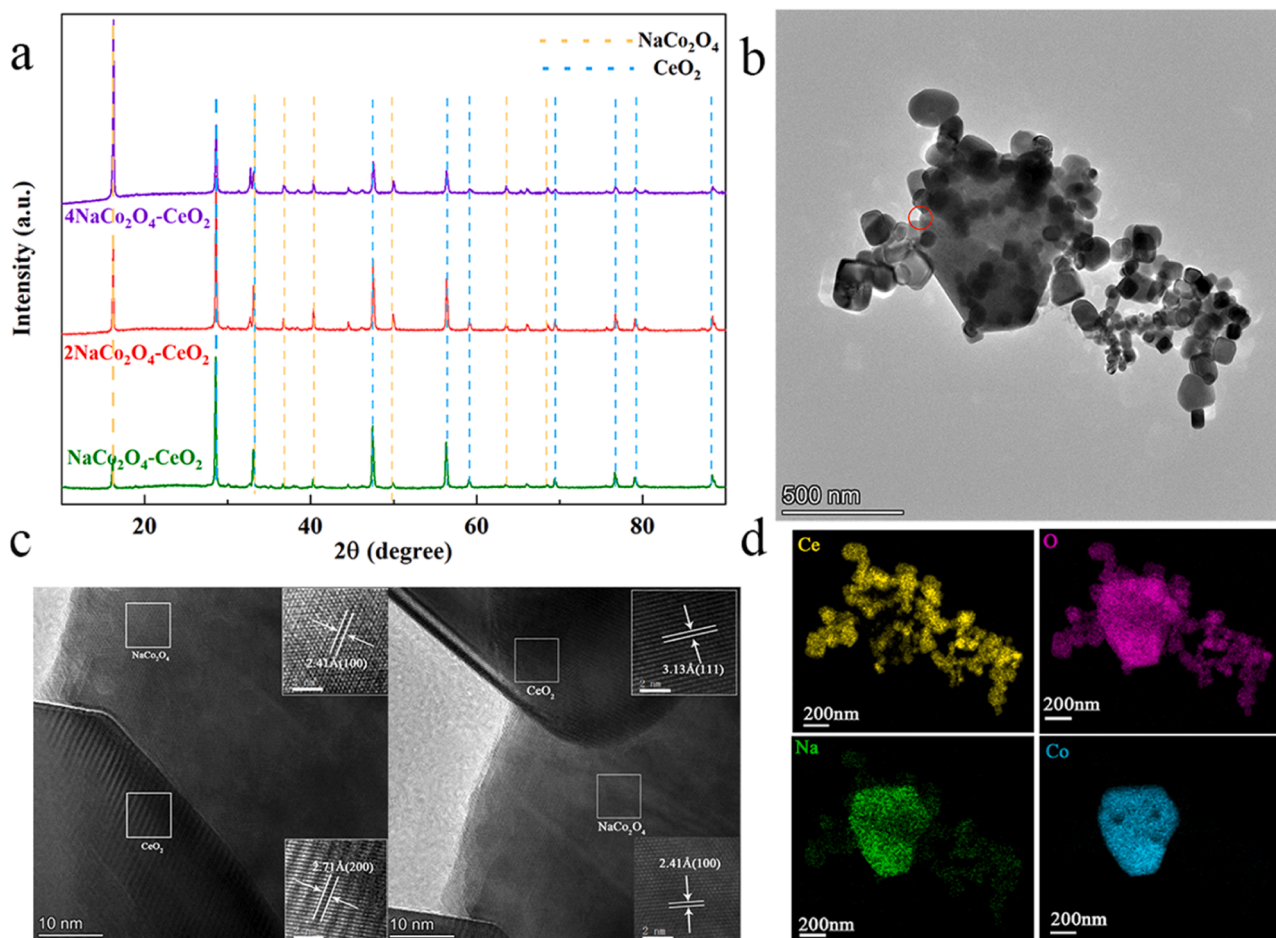
$$E_{\text{ads}} = E_{\text{adsorbate}} - E_{\text{e}} - E_{\text{adsorbate}}$$

Where  $E_{\text{adsorbate}}$  and  $E_{\text{e}}$  are the total energy of the surface with and without adsorbates, respectively.  $E_{\text{adsorbate}}$  represents the total energy of the adsorbate in the gas phase.

## 3. Results and discussion

### 3.1. Characterization of $x\text{NaCo}_2\text{O}_4/\text{CeO}_2$

The XRD spectrum of the  $x\text{NaCo}_2\text{O}_4/\text{CeO}_2$  are shown in Fig. 1a, the peaks at  $28.5^\circ$ ,  $47.4^\circ$  and  $56.3^\circ$ , corresponding to (111), (220) and (311) planes of  $\text{CeO}_2$  (PDF#43-1002), respectively [15]. Peaks at  $16.3^\circ$ ,  $33.1^\circ$  and  $50.0^\circ$  correspond to (002), (004) and (104) planes of  $\text{NaCo}_2\text{O}_4$  (PDF#27-0682) are also identified [16]. No other oxides related to Na are found in the XRD spectrum, except for  $\text{NaCo}_2\text{O}_4$ . TEM image of  $2\text{NaCo}_2\text{O}_4/\text{CeO}_2$  (Fig. 1b) illustrates that two-phase catalyst are composite through the manufacturing process. The TEM image of  $\text{CeO}_2$  and  $\text{NaCo}_2\text{O}_4$  from Fig. S1 and Fig. S2 could help to identify two species, the large sheet like structure is  $\text{NaCo}_2\text{O}_4$  and the spherical species are  $\text{CeO}_2$ . Comparing with single phase, the morphology of  $2\text{NaCo}_2\text{O}_4/\text{CeO}_2$  are similar comparing with  $\text{CeO}_2$  and  $\text{NaCo}_2\text{O}_4$  in TEM, which indicates that there was no phase change occurred between  $\text{CeO}_2$  and  $\text{NaCo}_2\text{O}_4$  during the production process. The  $\text{NaCo}_2\text{O}_4/\text{CeO}_2$  and  $4\text{NaCo}_2\text{O}_4/\text{CeO}_2$  image



**Fig. 1.** Structural characterizations of  $x\text{NaCo}_2\text{O}_4/\text{CeO}_2$ . (a) XRD patterns of  $x\text{NaCo}_2\text{O}_4/\text{CeO}_2$ . (b) TEM image of  $2\text{NaCo}_2\text{O}_4/\text{CeO}_2$ . (c) TEM images for  $2\text{NaCo}_2\text{O}_4/\text{CeO}_2$  from the red circle in Fig. 1b. (d) EDS element mapping of  $2\text{NaCo}_2\text{O}_4/\text{CeO}_2$ .



could find in Fig. S3 and Fig. S4, the morphology of them also stay the same with  $2\text{NaCo}_2\text{O}_4/\text{CeO}_2$ , illustrates that the change of  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  only alter the proportion of catalysts. For  $2\text{NaCo}_2\text{O}_4/\text{CeO}_2$ , TEM image shows the (111) and (200) crystal planes exposed to  $\text{CeO}_2$  and the (100) crystal planes corresponding to  $\text{NaCo}_2\text{O}_4$  (Fig. 1c) [17, 18]. The EDS results of  $2\text{NaCo}_2\text{O}_4/\text{CeO}_2$  also prove this inference (Fig. 1d). Furthermore, the EDS image not only shows the distribution of Na in the center of the catalysts, but also shows in the  $\text{CeO}_2$ , which indicates that the Na was distributed on all the catalysts in the beginning of catalysts manufacturing process.

### 3.2. The electro-performance of catalysts toward $\text{C}_2\text{H}_6$ OR

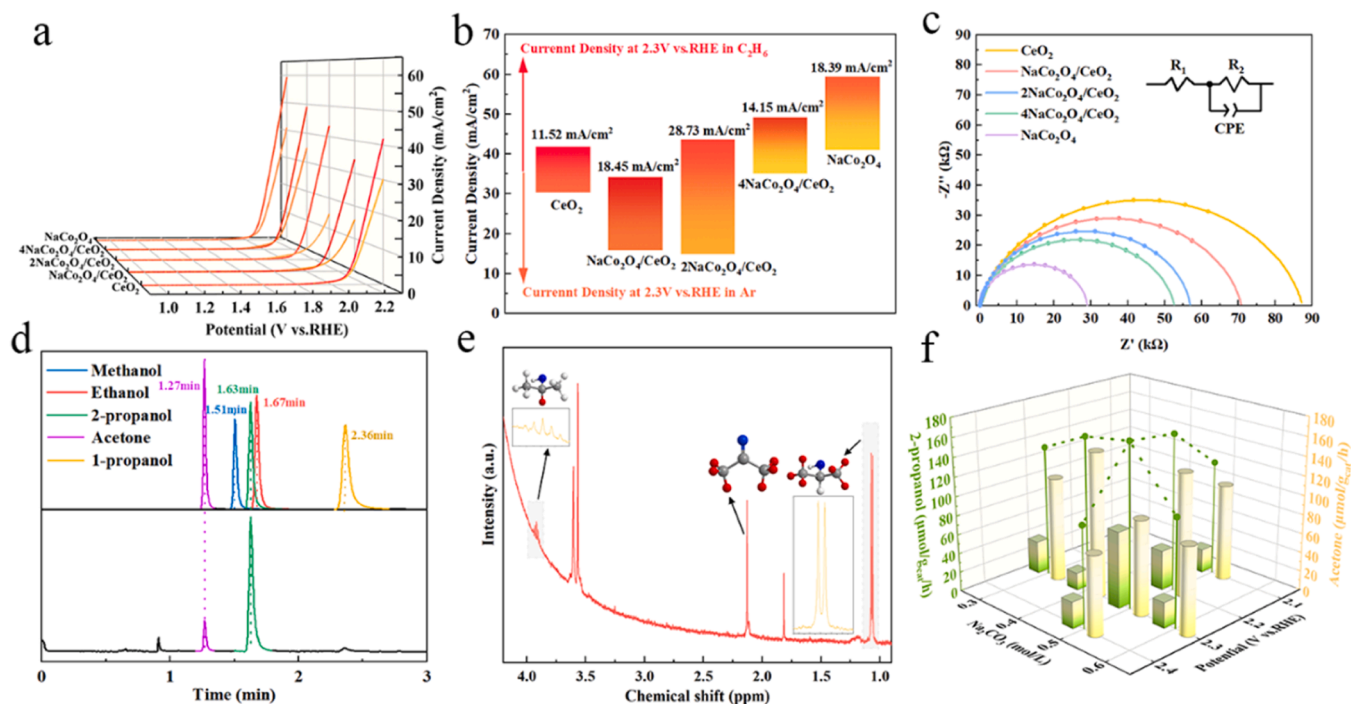
To test the  $\text{C}_2\text{H}_6$  OR performance of ethane, the LSV curves for five catalysts dispensed on carbonate electrolyte in  $\text{C}_2\text{H}_6$  and Ar-saturated  $\text{Na}_2\text{CO}_3$  solution are shown in Fig. 2a. The current density difference between two curves in the same potential is the key parameter to evaluate the capability of  $\text{C}_2\text{H}_6$ OR (Fig. 2b) [6]. The  $2\text{NaCo}_2\text{O}_4/\text{CeO}_2$  exhibits the highest current density difference in three composite catalysts. In addition, the  $\text{NaCo}_2\text{O}_4$  and  $\text{CeO}_2$  both exhibits the  $\text{C}_2\text{H}_6$ OR capability. Besides, comparing with the current density contrast of two single-phase catalysts, the current density difference of  $\text{CeO}_2$  is lower than that of  $\text{NaCo}_2\text{O}_4$ . This result not only shows high  $\text{C}_2\text{H}_6$  oxide capability, but also reveals strong synergistic effect between  $\text{NaCo}_2\text{O}_4$  and  $\text{CeO}_2$ . Except current density, good conductivity could also reflect the performance of catalysts [19]. EIS was tested in 1.7 V (vs.RHE) as the EIS results shows that  $\text{CeO}_2$  has the worst electronic conduction and highest ohmic resistance,  $\text{NaCo}_2\text{O}_4$  is on the contrary (Fig. 2c). According to the ICP (Table S1) and TEM results, even if  $\text{NaCo}_2\text{O}_4/\text{CeO}_2$  has similar proportion comparing with  $4\text{NaCo}_2\text{O}_4/\text{CeO}_2$ , the electrochemical performance including electronic conduction and current density is the worst in three catalysts, which could attribute to agglomerated in the process of preparation identified by TEM graph. For  $2\text{NaCo}_2\text{O}_4/\text{CeO}_2$  and  $4\text{NaCo}_2\text{O}_4/\text{CeO}_2$ ,  $\text{NaCo}_2\text{O}_4$  could promote electronic conductivity, also,  $\text{CeO}_2$  is distributed in the surface of  $\text{NaCo}_2\text{O}_4$ .

In this case, the electronic conductivity is better than that of  $\text{NaCo}_2\text{O}_4/\text{CeO}_2$ . In conclusion, the  $2\text{NaCo}_2\text{O}_4/\text{CeO}_2$  has the best  $\text{C}_2\text{H}_6$ OR capability in all five catalysts.

### 3.3. $\text{C}_2\text{H}_6$ conversion and product analysis

Carbon cloth electrode was made by five catalysts respectively. At first, all catalysts were used to convert  $\text{C}_2\text{H}_6$  in 2.3 V (vs.RHE) for 6 h in 0.5 mol/L  $\text{Na}_2\text{CO}_3$  solution, blank and 6 h sample were tested by GC, only  $2\text{NaCo}_2\text{O}_4/\text{CeO}_2$  and  $4\text{NaCo}_2\text{O}_4/\text{CeO}_2$  have products and the products content of  $4\text{NaCo}_2\text{O}_4/\text{CeO}_2$  is far less than  $2\text{NaCo}_2\text{O}_4/\text{CeO}_2$  (Fig. S5), which is corresponding to the LSV and EIS results. Besides, the products of  $\text{C}_2\text{H}_6$ OR were tested by GC and  $^1\text{H}$  NMR. At first, inject all possible substances into GC to obtain a determined peak time, corresponding to the peak of products. The results are compared in Fig. 2d. From these results, the products are all 2-propanol and acetone, whereas, there are no products detected under Ar. Fig. 2e shows the  $^1\text{H}$  NMR result of product sample in 2.3 V (vs.RHE), the  $\delta 3.92$  (m, 1 H) and  $\delta 1.08$  (d, 3 H) are attribute to 2-propanol, and the  $\delta 2.13$  (s, 3 H) is attribute to acetone [20,21]. The result of  $^1\text{H}$  NMR is corresponding to the GC results, which could confirm the main products of  $\text{C}_2\text{H}_6$  OR. The out gas was also collected and analyzed by GC, the results are shown in Fig. S6,  $\text{CO}_2$  was produced in the reaction process.

To investigate the formation process of acetone, 10  $\mu\text{L}$  of 2-propanol was added to 22 mL  $\text{Na}_2\text{CO}_3$  solution for 6 h, and the results are shown in Fig. S7, indicating that acetone is produced by the conversion of 2-propanol. From this result, all products could regard as 2-propanol to calculate the total products converted by ethane. As the best catalysts among five catalysts,  $2\text{NaCo}_2\text{O}_4/\text{CeO}_2$  was used to convert  $\text{C}_2\text{H}_6$  in different potential from 2 V (vs.RHE) to 2.4 V (vs.RHE) for 6 h. The total 2-propanol have a great rising from 120.11  $\mu\text{mol/g}_{\text{cat}}/\text{hr}$  in 2.1 V (vs. RHE) to 169.46  $\mu\text{mol/g}_{\text{cat}}/\text{hr}$  in 2.3 V (vs.RHE), however, the yield was declined to 103.82  $\mu\text{mol/g}_{\text{cat}}/\text{hr}$  in 2.4 V (vs.RHE) shown in Fig. 2f and Table S2. The results are attribute to the current density difference of  $2\text{NaCo}_2\text{O}_4/\text{CeO}_2$  in different potential (Fig. S8).



**Fig. 2.** (a) LSV curves of five catalysts in both Ar and  $\text{C}_2\text{H}_6$ -saturated  $\text{Na}_2\text{CO}_3$  solution. (b) the current density difference in 2.3 V (vs.RHE) of five catalysts. (c) EIS results of five catalysts in 1.7 V (vs.RHE), from 100,000 Hz to 0.1 Hz. (d) GC results of peak time including product and possible products sampling in GC. (e)  $^1\text{H}$  NMR results of  $\text{C}_2\text{H}_6$  OR in 2.3 V (vs.RHE) after 6 h in 0.5 mol/L  $\text{Na}_2\text{CO}_3$  solution. (f) Product concentration from 2.1 V (vs.RHE) to 2.4 V (vs.RHE) in 0.5 mol/L  $\text{Na}_2\text{CO}_3$  solution and the concentration from 0.3 mol/L to 0.6 mol/L  $\text{Na}_2\text{CO}_3$  solution in 2.3 V (vs.RHE).

### 3.4. Catalyst synthesis mechanism and active sites

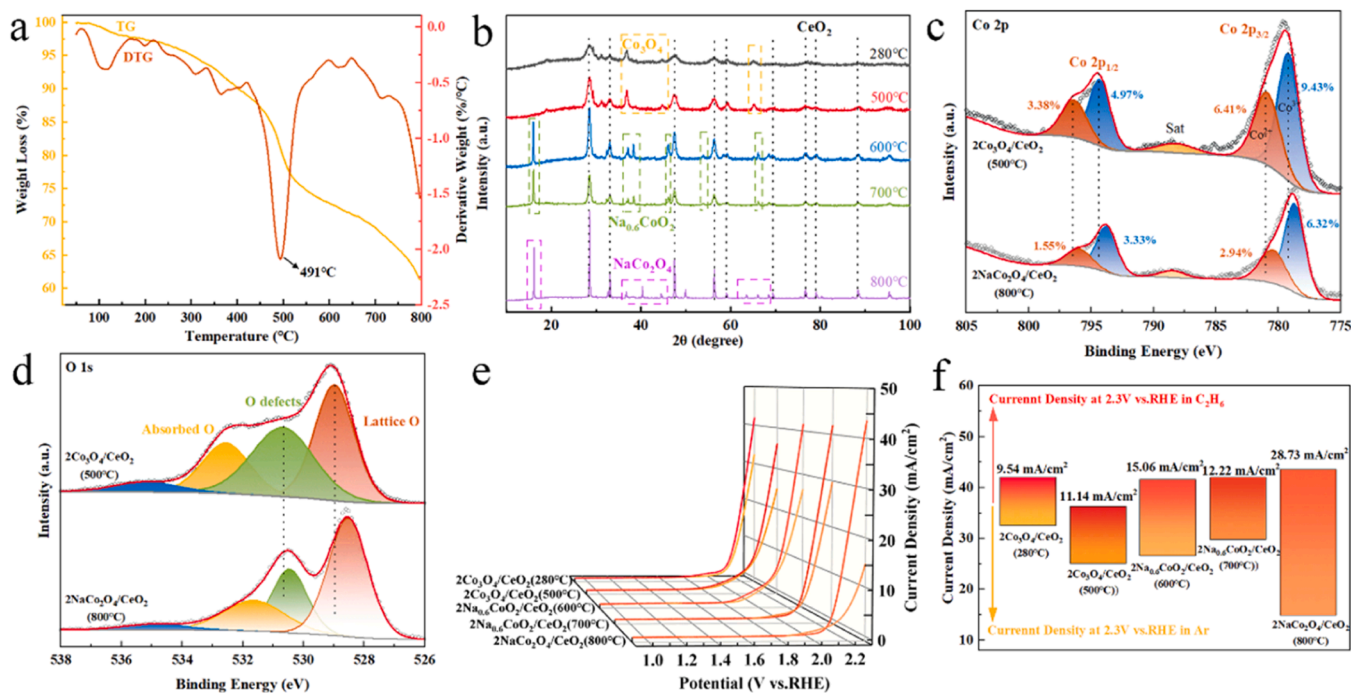
To further explain the process of the formation of the catalysts, the pre-calcined products and catalysts in different temperature of  $2\text{NaCo}_2\text{O}_4/\text{CeO}_2$  was tested by TG and XRD (Fig. 3a, b). The pre-calcined products and the temperature less than  $500^\circ\text{C}$  composited by  $\text{Co}_3\text{O}_4$  and  $\text{CeO}_2$  are denoted as  $2\text{Co}_3\text{O}_4/\text{CeO}_2$  and  $2\text{Co}_3\text{O}_4/\text{CeO}_2(500^\circ\text{C})$ . After increasing temperature from  $500^\circ\text{C}$  to  $700^\circ\text{C}$ , the main products denoted as  $2\text{Na}_{0.6}\text{CoO}_2/\text{CeO}_2$  are  $\text{Na}_{0.6}\text{CoO}_2$  and  $\text{CeO}_2$ . Finally, the products became  $2\text{NaCo}_2\text{O}_4/\text{CeO}_2$ . By comparing the XPS results of  $2\text{Co}_3\text{O}_4/\text{CeO}_2(500^\circ\text{C})$  and  $2\text{NaCo}_2\text{O}_4/\text{CeO}_2$ . The binding energy of Co 2p, O 1s and Na 1s are shown in Fig. 3c and Fig. 3d, Fig. S9 and Table S3. The binding energy of Ce 3d had no obvious change in the process of calcine. Combining with XRD results,  $\text{CeO}_2$  was not influenced by Na. For  $2\text{Co}_3\text{O}_4/\text{CeO}_2$ , it could be seen that the Co  $2p_{3/2}$  peak can be fitted into  $\text{Co}^{3+}$  and  $\text{Co}^{2+}$  components at the binding energy of 779.3 eV and 780.8 eV, respectively. The Co  $2p_{3/2}$  peak of  $2\text{NaCo}_2\text{O}_4/\text{CeO}_2$  in 778.7 eV and 780.4 eV could be attribute to  $\text{Co}^{3+}$  and  $\text{Co}^{2+}$  [22,23]. A shift of 0.4 eV occurred after introducing Na in  $\text{Co}_3\text{O}_4$ , which results in redistribution of interfacial charges. Furthermore, the ratio of  $\text{Co}^{3+}/\text{Co}^{2+}$  increased from 1.47 to 2.62 (Table S3) after Na was introduced, which illustrates that with the increasing of the temperature, there was a great change occurred in  $\text{Co}_3\text{O}_4$  and new phase produced. According to the crystal structure of  $\text{NaCo}_2\text{O}_4$ , the increase of  $\text{Co}^{3+}$  represents more lattice O produced and the  $\text{Co}^{2+}$  could attribute to O defects in the surface of  $\text{NaCo}_2\text{O}_4$ . Besides, the O 1s of  $2\text{Co}_3\text{O}_4/\text{CeO}_2$  and  $2\text{NaCo}_2\text{O}_4/\text{CeO}_2$  can be deconvoluted into four peaks. The peaks of 528.9 eV and 528.5 eV could attribute to lattice O, the peaks in 530.7 eV and 530.4 eV could bind to O defect. Furthermore, comparing with  $2\text{Co}_3\text{O}_4/\text{CeO}_2$  and  $2\text{NaCo}_2\text{O}_4/\text{CeO}_2$ , the ratio of lattice O/O defects have a great raise from 1.07 to 1.75. The introduce of Na recrystallized  $\text{Co}_3\text{O}_4$  to form a new phase, thereby increasing the amount of lattice oxygen and reduced the content of O defects.

To investigate the resource of Na, the EDTA-2Na was exchanged to EDTA in the manufacturing process of  $2\text{NaCo}_2\text{O}_4/\text{CeO}_2$ . The XRD pattern was shown in Fig. S10, the final product was  $\text{Co}_3\text{O}_4/\text{CeO}_2$ . From

these results, it is confirmed that Na is dispersed in products because of the EDTA-2Na. Furthermore, to investigate the existing state of Na, the XPS results of Na 1s between  $2\text{Co}_3\text{O}_4/\text{CeO}_2(500^\circ\text{C})$  and  $\text{NaCo}_2\text{O}_4$  are compared, there is only 0.1 eV shift in binding energy, however, there are no Na oxide exist in XRD pattern in Fig. 3b. Finally, from the EDS results of  $2\text{NaCo}_2\text{O}_4/\text{CeO}_2$  in Fig. 1(d), the Na in  $\text{CeO}_2$  was dispersed but not gathered as Co or Ce elements. In this case, the Na are amorphous form in low temperature ( $280^\circ\text{C}$ ,  $500^\circ\text{C}$ ). These two catalysts  $2\text{Co}_3\text{O}_4/\text{CeO}_2(500^\circ\text{C})$  and  $\text{Co}_3\text{O}_4/\text{CeO}_2$  was also used for  $\text{C}_2\text{H}_6$  conversion in 2.3 V(vs.RHE), however, there was no product tested by GC.

The XPS results of  $2\text{NaCo}_2\text{O}_4/\text{CeO}_2$  are also compared with  $\text{CeO}_2$  and  $\text{NaCo}_2\text{O}_4$  and shown in Fig. S11. The Co  $2p_{3/2}$  peak can be fitted into  $\text{Co}^{3+}$  and  $\text{Co}^{2+}$  components at the binding energy of 779.3 eV and 780.8 eV, respectively. According to Table S3, the ratio of  $\text{Co}^{3+}/\text{Co}^{2+}$  in  $2\text{NaCo}_2\text{O}_4/\text{CeO}_2$  increased comparing with  $\text{NaCo}_2\text{O}_4$ . Furthermore, the O 1s and Na 1s has changed after the combination of  $\text{NaCo}_2\text{O}_4$  and  $\text{CeO}_2$ . The Na 1s of  $2\text{NaCo}_2\text{O}_4/\text{CeO}_2$  also occurs a peak in 1068.8 eV (Fig. S11). The lower binding energy of Na 1s may come from the combination between  $\text{NaCo}_2\text{O}_4$  and  $\text{CeO}_2$ , which could illustrate that the Na not only changed the  $\text{Co}_3\text{O}_4$  but also connected  $\text{NaCo}_2\text{O}_4$  and  $\text{CeO}_2$ . For O 1s, the ratio of lattice O/O defects in  $2\text{NaCo}_2\text{O}_4/\text{CeO}_2$  is more than single-phase, which indicates that it is different in the process of catalysts preparation. If  $\text{NaCo}_2\text{O}_4$  and  $\text{CeO}_2$  are prepared individually, there would be more O defects, however, co synthesis could produce more lattice O. The reason for this phenomenon would indicates that the co-synthesis made more  $\text{CeO}_2$  composite with  $\text{NaCo}_2\text{O}_4$  and covered more defects.

To explore the connection between catalyst changes and electrochemical conversion capability, all catalysts formed in manufacturing process was tested by LSV. At first,  $2\text{NaCo}_2\text{O}_4/\text{CeO}_2$  was used to test the LSV curves in different solution and the results are shown in Fig. S12. Comparing with  $\text{Na}_2\text{CO}_3$ , 0.5 mol/L  $\text{Na}_2\text{SO}_4$  solution has same concentration of both  $\text{Na}^+$  and anion. However, there is a huge gap in current density in 2.3 V(vs.RHE) between two solutions, which means the ion concentration in solution is not a determining factor of current density. Besides, the 0.5 mol/L  $\text{Na}_2\text{CO}_3$  solution was tested by Acidimeter, the



**Fig. 3.** (a) TG curves of  $2\text{NaCo}_2\text{O}_4/\text{CeO}_2$  at a heating rate of  $5^\circ\text{C}$ . (b) XRD patterns of  $2\text{NaCo}_2\text{O}_4/\text{CeO}_2$  precursor calcined in different temperatures. (c) XPS results of Co 2p spectra for  $2\text{Co}_3\text{O}_4/\text{CeO}_2$  and  $2\text{NaCo}_2\text{O}_4/\text{CeO}_2$ . (d) XPS results O 1s spectra for  $2\text{Co}_3\text{O}_4/\text{CeO}_2$  and  $2\text{NaCo}_2\text{O}_4/\text{CeO}_2$ . (e) LSV curves of  $2\text{NaCo}_2\text{O}_4/\text{CeO}_2$  precursor calcined in different temperatures. (f) the current density difference in 2.3 V(vs.RHE) of precursors.

result was pH=11.4. The NaOH solution in the same pH was made and tested to investigate whether the OER dominated in reaction process, the LSV curve was almost same comparing with Na<sub>2</sub>SO<sub>4</sub> solution, illustrates that OER is not the main reaction in Na<sub>2</sub>CO<sub>3</sub> solution. Therefore, the LSV results tested after Ar-saturated is the CO<sub>3</sub><sup>2-</sup> OR and convert it to O<sup>2-</sup> and CO<sub>2</sub> [6,19]. After using the 2NaCo<sub>2</sub>O<sub>4</sub>/CeO<sub>2</sub> by chronoamperometry (CA) to convert ethane in different solutions (Fig. S13), it was found that only Na<sub>2</sub>CO<sub>3</sub> solution exists products, which demonstrates that O<sup>2-</sup> is essential in ethane conversion. Furthermore, the current density difference of five catalysts in different calcination temperatures in 2.3 V(vs. RHE) are shown in Fig. 3e and Fig. 3f, the CO<sub>3</sub><sup>2-</sup> OR capability of 2NaCo<sub>2</sub>O<sub>4</sub>/CeO<sub>2</sub> is the worst. Combining with the XPS results of O 1 s, Co 2p and product results of five catalysts after C<sub>2</sub>H<sub>6</sub> OR process, the ratio of O defects also declined, which indicates that O defects are the main active site for CO<sub>3</sub><sup>2-</sup> OR. To further illustrate the changes in O defects, EPR was also tested, the results are shown in Fig. S14, the O defects became less after 2Co<sub>3</sub>O<sub>4</sub>/CeO<sub>2</sub>(500 °C) was changed to 2NaCo<sub>2</sub>O<sub>4</sub>/CeO<sub>2</sub>. The 2NaCo<sub>2</sub>O<sub>4</sub>/CeO<sub>2</sub> also has less defects comparing with 4NaCo<sub>2</sub>O<sub>4</sub>/CeO<sub>2</sub>, which is corresponding with the amount of production between these two catalysts in 2.3 V(vs.RHE) [24]. Besides, the C<sub>2</sub>H<sub>6</sub> OR capability also increased after 2Co<sub>3</sub>O<sub>4</sub>/CeO<sub>2</sub> was converted to 2NaCo<sub>2</sub>O<sub>4</sub>/CeO<sub>2</sub>, through this process, the ratio of Co<sup>3+</sup>/Co<sup>2+</sup> also increased, which could illustrate that lattice O is the main factor for C<sub>2</sub>H<sub>6</sub> OR.

To explore the function of CeO<sub>2</sub>, the substantial differences in the redox properties and CO<sub>3</sub><sup>2-</sup> OR performances of all catalysts except NaCo<sub>2</sub>O<sub>4</sub>/CeO<sub>2</sub> on glassy carbon electrode are shown by cyclic voltammetry (CV) recorded in 0.5 mol/L Na<sub>2</sub>CO<sub>3</sub> solution (Fig. S15). Two sets of pre-CO<sub>3</sub><sup>2-</sup> OR redox features are observed in 2NaCo<sub>2</sub>O<sub>4</sub>/CeO<sub>2</sub>, 4NaCo<sub>2</sub>O<sub>4</sub>/CeO<sub>2</sub> and NaCo<sub>2</sub>O<sub>4</sub>. The redox peaks have no occurrence in CV curves of CeO<sub>2</sub>, which could indicate that the redox peaks in other three catalysts are attribute to NaCo<sub>2</sub>O<sub>4</sub>. The reversible processes may be assigned to cobalt redox species involving Co<sup>III</sup>/Co<sup>II</sup> and Co<sup>IV</sup>/Co<sup>III</sup> couples, respectively [25–28]. With the increasing content of CeO<sub>2</sub>, the redox potential of NaCo<sub>2</sub>O<sub>4</sub> is also increasing, which could indicate that the CeO<sub>2</sub> could improve the stability of the catalyst by increasing the redox potential of NaCo<sub>2</sub>O<sub>4</sub>.

To test the stability of the 2NaCo<sub>2</sub>O<sub>4</sub>/CeO<sub>2</sub>, the carbon cloth loaded with catalyst was compared before and after 6 h of C<sub>2</sub>H<sub>6</sub> conversion. From the XRD pattern in Fig. S16, both NaCo<sub>2</sub>O<sub>4</sub> and CeO<sub>2</sub> peaks were declined because of the catalyst was detached. However, there was no change in XRD pattern, which could illustrate that the catalyst is stable. From the XPS results in Fig. S17, there was a small shift occurred after 6 h. There was an increase in the number of lattice O/O defects from 1.75 in origin to 2NaCo<sub>2</sub>O<sub>4</sub>/CeO<sub>2</sub> after 6 h. However, the number of Co<sup>3+</sup>/Co<sup>2+</sup> had a decrease from 2.62 to 1.67, which could attribute to partial damage occurred on the surface of NaCo<sub>2</sub>O<sub>4</sub>. The reason may form the O<sup>2-</sup> produced from CO<sub>3</sub><sup>2-</sup>. This phenomenon illustrates that the increase of the lattice O most came from the CeO<sub>2</sub>.

As a result, the mechanism of ethane electrocatalytic conversion on catalysts is that the interface between NaCo<sub>2</sub>O<sub>4</sub> and CeO<sub>2</sub> created a good environment for the O defects mainly responsible for CO<sub>3</sub><sup>2-</sup> OR to decline energy barrier for C<sub>2</sub>H<sub>6</sub> OR, afterwards, the C<sub>2</sub>H<sub>6</sub> was activated by lattice O on 2NaCo<sub>2</sub>O<sub>4</sub>/CeO<sub>2</sub> and oxidized through CO<sub>3</sub><sup>2-</sup> OR.

### 3.5. The competition of C<sub>2</sub>H<sub>6</sub> OR and CO<sub>3</sub><sup>2-</sup> OR

It is known that CO<sub>3</sub><sup>2-</sup> is easier to be oxidized comparing with C<sub>2</sub>H<sub>6</sub>. In this case, it is vital to explore the competition between C<sub>2</sub>H<sub>6</sub> OR and CO<sub>3</sub><sup>2-</sup> OR. As the results above, the 2-propanol in 2.3 V(vs.RHE) has the most content. To test the competition between CO<sub>3</sub><sup>2-</sup> OR and C<sub>2</sub>H<sub>6</sub> OR and find suitable solution concentration, 2NaCo<sub>2</sub>O<sub>4</sub>/CeO<sub>2</sub> was used in 0.1–0.6 mol/L Na<sub>2</sub>CO<sub>3</sub> solution at 2.3 V(vs.RHE), the results are also shown in Fig. 2f. The reason for the absence of products at 0.1–0.2 mol/L is that insufficient CO<sub>3</sub><sup>2-</sup> could not supply enough O<sup>2-</sup>. The total 2-propanol production is raising from 136.67 to 169.46 μmol/g<sub>cat</sub>/hr with the

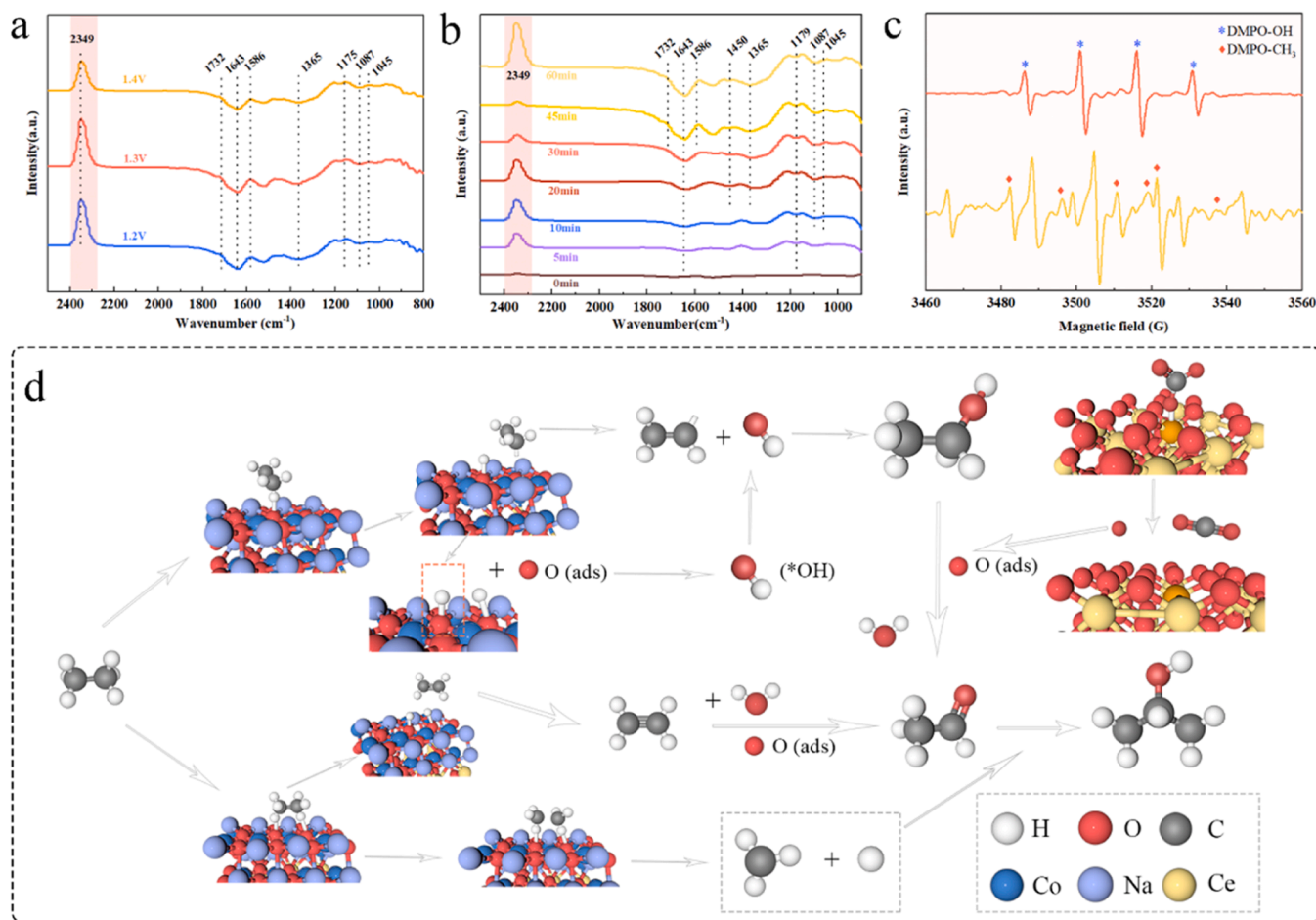
increasing solution concentration and suddenly cut down to 111.31 μmol/g<sub>cat</sub>/hr in 0.6 mol/L Na<sub>2</sub>CO<sub>3</sub>, this may attribute to excessive CO<sub>3</sub><sup>2-</sup> suppressed ethane conversion. The highest selectivity of acetone reaches 89 % at 2.3 V(vs.RHE) in 0.4 mol/L Na<sub>2</sub>CO<sub>3</sub> solution. The most product yield was at 2.3 V(vs.RHE) in 0.5 mol/L Na<sub>2</sub>CO<sub>3</sub> solution. From these results, excessive energy supply and CO<sub>3</sub><sup>2-</sup> concentration could lead to the competition of two reaction. The CO<sub>3</sub><sup>2-</sup> OR capability of five catalysts is shown in Fig. S18. The NaCo<sub>2</sub>O<sub>4</sub> and CeO<sub>2</sub> have no products may also attribute to high O defects content lead to the excessive competition of CO<sub>3</sub><sup>2-</sup> OR. Furthermore, this conclusion could also infer that the CO<sub>3</sub><sup>2-</sup> OR could not convert C<sub>2</sub>H<sub>6</sub> individually. The C<sub>2</sub>H<sub>6</sub> OR is the synergistic effect of both CO<sub>3</sub><sup>2-</sup> OR on defects and the lattice O in NaCo<sub>2</sub>O<sub>4</sub>. In addition, comparing the Tafel slope of three composite materials after introducing Ar and ethane, the Tafel slope of 2NaCo<sub>2</sub>O<sub>4</sub>/CeO<sub>2</sub> and 4NaCo<sub>2</sub>O<sub>4</sub>/CeO<sub>2</sub> in Ar indicates that it is more difficult to oxidize CO<sub>3</sub><sup>2-</sup> in the weak polarized region (Fig. S19–21). As the voltage increases, CO<sub>3</sub><sup>2-</sup> OR in the strong polar region increases [6]. However, after introducing ethane, the Tafel slope increases, which attribute to more difficulty for chemical reaction as C<sub>2</sub>H<sub>6</sub> OR is introduced into the overall reaction process. The Tafel slope of 4NaCo<sub>2</sub>O<sub>4</sub>/CeO<sub>2</sub> shows less variation compared to 2NaCo<sub>2</sub>O<sub>4</sub>/CeO<sub>2</sub> in the strongly polarized region, indicating that ethane participates less in the overall reaction, corresponding to a lower yield of products at 2.3 V(vs.RHE). For NaCo<sub>2</sub>O<sub>4</sub>/CeO<sub>2</sub>, the Tafel slope did not increase in strong polarized region after the addition of ethane, indicating that ethane did not participate in the overall reaction.

To investigate the importance of CO<sub>3</sub><sup>2-</sup> OR, 10 μL 2-propanol was also added in 0.5 mol/L Na<sub>2</sub>SO<sub>4</sub> solution and the result is compared with result in 0.5 mol/L Na<sub>2</sub>CO<sub>3</sub> in Fig. S22. The content of acetone in 0.5 mol/L Na<sub>2</sub>SO<sub>4</sub> solution has a significant decline comparing with 0.5 mol/L Na<sub>2</sub>CO<sub>3</sub> solution, which indicates that the production of acetone is mainly from the effect of CO<sub>3</sub><sup>2-</sup> OR. In addition, the HER process occurred on counter electrode have no promoting effect on oxidation reaction. This result could also confirm that the CO<sub>3</sub><sup>2-</sup> OR is the only reaction that promote the process of C<sub>2</sub>H<sub>6</sub> OR.

To study the C<sub>2</sub>H<sub>6</sub> OR mechanism on the 2NaCo<sub>2</sub>O<sub>4</sub>/CeO<sub>2</sub> surface, in situ ATR-FTIR and EPR experiments were carried out to record the intermediate products in the process of producing 2-propanol. Fig. 4a shows the spectra collected in different potentials from 2.1 to 2.3 V(vs. RHE) after reacted 60 min. All three peaks are almost same, which indicates that the reaction process are same even if the potential are different. The bands at 1045 cm<sup>-1</sup> and 1087 cm<sup>-1</sup> could be assigned to C-OH and C-O stretching vibration in ethanol [29,30]. Besides, the band in 1365 cm<sup>-1</sup> and 1179 cm<sup>-1</sup> are the C-H and C-C deformation vibration of 2-propanol, respectively [31,32]. Afterwards, the band at 1732 cm<sup>-1</sup> and 1643 cm<sup>-1</sup> could attribute to C=O stretching vibration of acetaldehyde and symmetric stretching vibration of C=C in C<sub>2</sub>H<sub>4</sub> [31,33]. Finally, the band in 2349 cm<sup>-1</sup> is corresponding to asymmetrical stretching vibration of CO<sub>2</sub> [30]. For band in 2349 cm<sup>-1</sup>, the intensity of CO<sub>2</sub> is weaker in 2.3 V(vs.RHE) than lower potential. This could be connected to the competition between CO<sub>3</sub><sup>2-</sup> OR and C<sub>2</sub>H<sub>6</sub> OR and the results are same. In 2.3 V(vs.RHE), CO<sub>3</sub><sup>2-</sup> OR is weaker results in more C<sub>2</sub>H<sub>6</sub> OR and the increase of products. It is proved that the 2-propanol appeared in catalyst successfully. Besides, ethanol (C–O, C–C), acetaldehyde (C=O), ethylene (C=C) and CO<sub>2</sub> were detected. These intermediate products recorded in Table 1 may go through further oxidation and serve as the stable intermediate to form the main products.

After confirming 2.3 V(vs.RHE) as the best potential of C<sub>2</sub>H<sub>6</sub> OR, time series ATR-FTIR spectra are obtained by fixing the electrode potential at 2.3 V(vs.RHE) and monitoring the spectra changes with reaction time (Fig. 4b). Some characteristic peaks appear (shown in Table 1) after the reaction begins and the intensity gradually grows with time increase. The peaks of CO<sub>2</sub> (2349 cm<sup>-1</sup>) had a gradual improve before 20 min, which indicates that the CO<sub>3</sub><sup>2-</sup> OR is the main reaction during this period of time. The band of ethanol in 1045 cm<sup>-1</sup> and 1087 cm<sup>-1</sup> was detected after 10 min and accumulating in the rest of





**Fig. 4.** (a) In situ ATR-FTIR results of 2NaCo<sub>2</sub>O<sub>4</sub>/CeO<sub>2</sub> in different potential after 1 h. (b) In situ ATR-FTIR results of 2NaCo<sub>2</sub>O<sub>4</sub>/CeO<sub>2</sub> at 2.3 V(vs.RHE) in different time periods. (c) In situ EPR results of 2NaCo<sub>2</sub>O<sub>4</sub>/CeO<sub>2</sub> in 2.3 V(vs.RHE). (d) Reaction pathway of C<sub>2</sub>H<sub>6</sub> conversion.

**Table 1**

ATR-FTIR absorbance bands and corresponding band assignments.

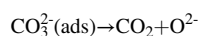
Frequency (cm <sup>-1</sup> )	Band assignment
1045	$\nu$ (C–OH) in ethanol
1087	$\nu$ (C–O) in ethanol
1179	$\delta$ (C–C) in 2-propanol
1365	$\delta_s$ (CH <sub>3</sub> ) in 2-propanol
1643	$\nu_s$ (C=C) in ethylene
1732	$\nu$ (C=O) in acetaldehyde
2349	$\nu_{as}$ (C=C) in CO <sub>2</sub>

time. The 2-propanol band in 1179 cm<sup>-1</sup> and 1365 cm<sup>-1</sup> occurred after ethanol was found, which could infer that 2-propanol is converted by ethanol as the intermediate. In 30 min and 45 min, as the CO<sub>3</sub><sup>2-</sup> OR declined, the C<sub>2</sub>H<sub>6</sub>OR occupied more oxidation processes since the intensity of CO<sub>2</sub> in 2349 cm<sup>-1</sup> declined but the intensity of C<sub>2</sub>H<sub>4</sub> in 1643 cm<sup>-1</sup> increased. In this case, there are two pathways for forming C<sub>2</sub>H<sub>4</sub> including C<sub>2</sub>H<sub>6</sub> was activated on the surface of NaCo<sub>2</sub>O<sub>4</sub> and ethanol was oxidized by O<sup>2-</sup>. After 45 min, the peak of acetaldehyde in 1732 cm<sup>-1</sup> was finally detected, which could infer that acetaldehyde was converted by ethanol and C<sub>2</sub>H<sub>4</sub> due to O<sup>2-</sup> oxidation. The reason why acetaldehyde was not occurred in 30 min may attribute to low content caused by insufficient ethanol and C<sub>2</sub>H<sub>4</sub>. After C<sub>2</sub>H<sub>4</sub> was accumulated sufficiently and acetaldehyde occurred, the peak of 2-propanol was also improved. From these results, the rate-limiting step could be inferred as the process that C<sub>2</sub>H<sub>4</sub> was converted to acetaldehyde as the direct changing relation between them.

To further investigate the formation process and the catalytic

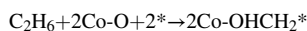
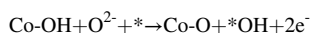
mechanism, 5,5-dimethyl-1-pyrroline N-oxide (DMPO) was used as a spin-trapping reagent for conducting EPR experiments. The ·CH<sub>3</sub> and ·OH was tested in 2.3 V(vs.RHE) after converting C<sub>2</sub>H<sub>6</sub> for 15 min. From the EPR results in Fig. 4c, there are ·CH<sub>3</sub> exist in the reaction process [34–36], which could verify that the C–C bond was broken. Besides, form the mechanism that methane conversion to ethanol or 2-propanol, the products originate from the coupling of methyl groups. The ·OH was also tested in the reaction process [37], this could be attributed to the combination of O<sup>2-</sup> and H from C<sub>2</sub>H<sub>6</sub>. From the 2-propanol conversion experiment, if the ·OH produced from the counter electrode, the 2-propanol should be converted easily in Na<sub>2</sub>SO<sub>4</sub> solution. In this case, the ·OH should have a greater possibility that produced in CO<sub>3</sub><sup>2-</sup> OR process. This evidence could also explain the formation of ethanol.

Based on the ATR-FTIR spectra and EPR results, combining with the mechanism of adsorbate evolution mechanism (AEM) and the lattice oxygen mechanism (LOM) [38,39]. The process of C<sub>2</sub>H<sub>6</sub> OR activation in 2NaCo<sub>2</sub>O<sub>4</sub>/CeO<sub>2</sub> and the conversion of C<sub>2</sub>H<sub>5</sub>OH and CH<sub>2</sub>=CH<sub>2</sub> are all shown in Fig. 4d. Combining with the mechanism proposed by Jaehyun Lee [9] and the results obtained above, the CO<sub>3</sub><sup>2-</sup> was combined with the defects of CeO<sub>2</sub> and became CO<sub>2</sub> and O<sup>2-</sup> [6].

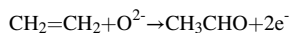


To explore the formation process of CH<sub>2</sub>=CH<sub>2</sub>. First, it is reported that C<sub>2</sub>H<sub>6</sub> could be dehydrogenated to C<sub>2</sub>H<sub>4</sub> [2,40]. In this case, The two H in C<sub>2</sub>H<sub>6</sub> may combine with two lattice O in Co–O to produce Co–OH and CH<sub>2</sub>=CH<sub>2</sub> [41]. Afterwards, the O<sup>2-</sup> from CO<sub>3</sub><sup>2-</sup> would combine with Co–OH to produce Co–O and ·OH. Also, due to the weaker C–C bond compared with the C–H bond, the C<sub>2</sub>H<sub>6</sub> could also be activated by Co–O

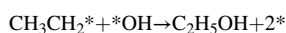
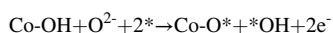
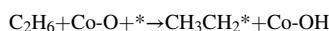
and produce  $\text{Co-OHCH}_2^*$  [3].



After  $\text{CH}_2=\text{CH}_2$  was produced, with the help of  $\text{O}^{2-}$  and  $\text{H}_2\text{O}$ , the  $\text{CH}_2=\text{CH}_2$  could be converted to  $\text{CH}_3\text{CHO}$  easily due to Wacker reaction [42].



For the formation mechanism of  $\text{C}_2\text{H}_5\text{OH}$ , the most possible way is  $\text{C}_2\text{H}_6$  activated on catalysts, the C-H bond combined with the lattice O on  $\text{NaCo}_2\text{O}_4$  to produce  $\text{Co-OH}$  and  $\text{CH}_3\text{CH}_2^*$ , then the  $\text{O}^{2-}$  attacked  $\text{Co-OH}$  to produce C-O and  $*\text{OH}$ , finally, the  $\text{CH}_3\text{CH}_2^*$  was combined with  $*\text{OH}$  and synthesized  $\text{C}_2\text{H}_5\text{OH}$  [6,8].



It is reported that  $\text{C}_2\text{H}_5\text{OH}$  could also be converted to  $\text{CH}_2=\text{CH}_2$  by electrocatalysis [33], this could explain the reason that the  $\text{CH}_2=\text{CH}_2$  peak is more and more strong in the reaction process.

Finally, the  $\text{CH}_3\text{CHO}$  combined with  $\text{CH}_3^*$  and H absorbed on Co-O to produce  $\text{CH}_3\text{CHOHCH}_3$ .



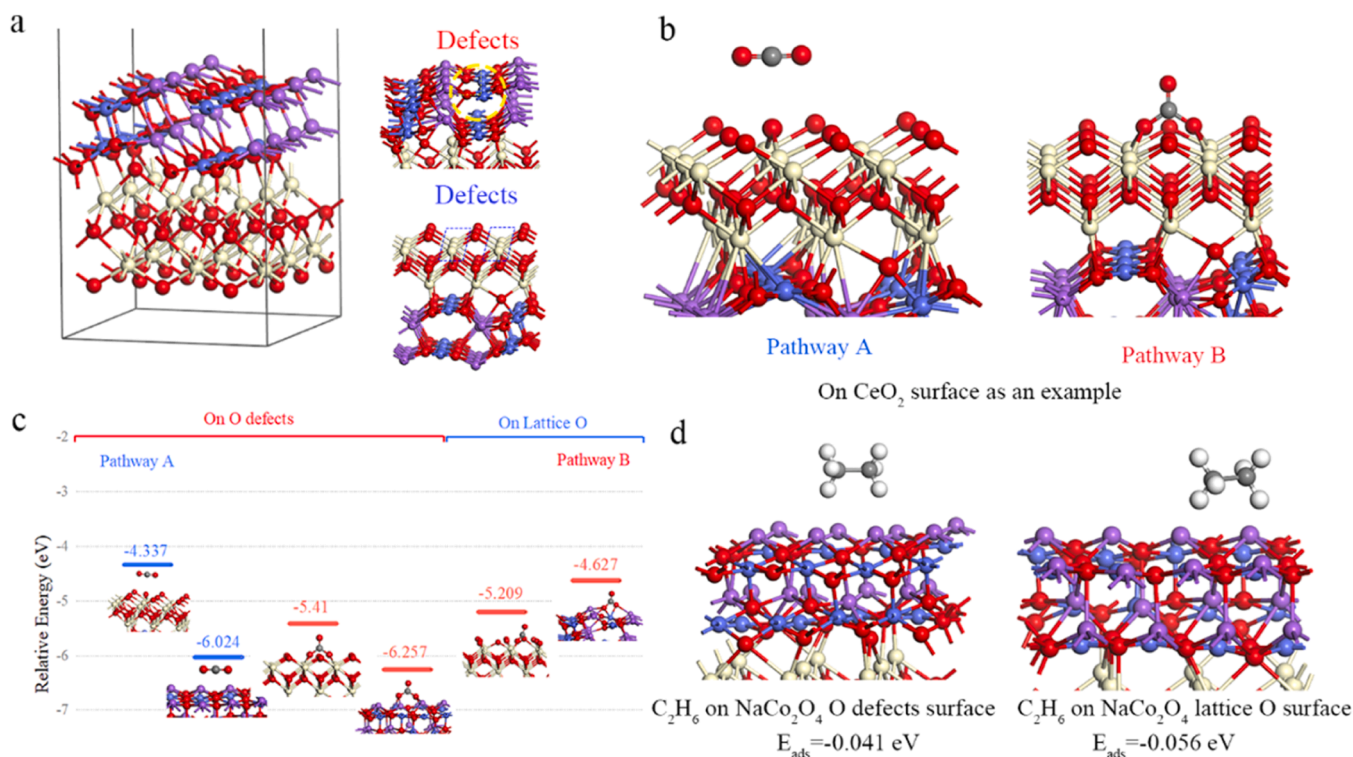
### 3.6. DFT calculation

To further understand the catalytic activity of the difference between

lattice O and O defects, DFT calculations were conducted by focusing on the energy changes of absorption and reaction of  $\text{CO}_3^{2-}$  on  $\text{CeO}_2$  and  $\text{NaCo}_2\text{O}_4$  surface. At first, the catalyst model of the  $2\text{NaCo}_2\text{O}_4$  (100) and  $\text{CeO}_2$  (100) was chosen as the exposed crystal plane and created O defects on both side (Fig. 5a). To explore the different possible adsorption pathway of  $\text{CO}_3^{2-}$ , one or two O atoms of  $\text{CO}_3^{2-}$  (Pathway A and B) adsorbed on both  $\text{NaCo}_2\text{O}_4$  and  $\text{CeO}_2$  surface were simulated (Fig. 5b). From Fig. 5c, the  $\text{CO}_3^{2-}$  adsorption energy ( $E_{\text{ads}}$ ) on  $\text{CeO}_2$  was decreased from  $-4.337$  eV to  $-5.410$  eV if two O atoms was absorbed on defects (Pathway B), the  $E_{\text{ads}}$  on  $\text{NaCo}_2\text{O}_4$  was also decreased from  $-6.0242$  eV to  $-6.257$  eV, which indicates that Pathway B is much easier comparing with Pathway A. These two different adsorption pathway also illustrate that the Pathway B could be the main reason for reaction promotion on  $\text{CO}_3^{2-}$  OR due to the exposed O (or  $\text{O}^{2-}$ ) on  $\text{CO}_3^{2-}$ . The other pathway could offer lattice O to activate  $\text{C}_2\text{H}_6$  and produce  $\text{CO}_2$ .

Moreover, both  $E_{\text{ads}}$  on  $\text{NaCo}_2\text{O}_4$  are lower than that of  $\text{CeO}_2$ , which could illustrate that  $\text{NaCo}_2\text{O}_4$  has a stronger  $\text{CO}_3^{2-}$  OR capability. This result is identical to Fig. 2b as the current density of  $\text{NaCo}_2\text{O}_4$  in  $\text{CO}_3^{2-}$  OR is higher than  $\text{CeO}_2$ . Furthermore, the adsorption reaction could occur on both  $\text{NaCo}_2\text{O}_4$  and  $\text{CeO}_2$ . In this case, the  $\text{CeO}_2$  could also participate on  $\text{CO}_3^{2-}$  OR thereby offer more opportunities for  $\text{C}_2\text{H}_6$  OR on  $\text{NaCo}_2\text{O}_4$  surface. In addition, from the in situ ATR-FTIR results, it can be seen that the reason for the decrease in  $\text{CO}_2$  intensity at 30 min in Fig. 4c may be due to the temporary occupation of defect sites by oxygen atoms, resulting in a decrease in  $\text{CO}_3^{2-}$  OR. Meanwhile, the intermediate products also began to accumulate after 30 min, proves that the lattice O accumulated and activated  $\text{C}_2\text{H}_6$ .

To investigate the competition of  $\text{CO}_3^{2-}$  between lattice O and O defects, the adsorption energy of  $\text{CO}_3^{2-}$  on lattice O was also calculated based on the more favorable Pathway B. From Fig. 5c, the  $E_{\text{ads}}$  on lattice O are both higher than that of O defects. The  $E_{\text{ads}}$  on the lattice O of  $\text{NaCo}_2\text{O}_4$  ( $-4.627$  eV) was also lower than Pathway A on O defects ( $-6.024$  eV), which illustrates that defects on  $\text{NaCo}_2\text{O}_4$  are the main active site for  $\text{CO}_3^{2-}$  OR. Furthermore,  $E_{\text{ads}}$  on the lattice O of  $\text{CeO}_2$  ( $-5.209$  eV) was even lower than Pathway A on O defects. As a result, the



**Fig. 5.** (a) The structure of  $2\text{NaCo}_2\text{O}_4/\text{CeO}_2$  in both crystal plane of (100). (b) Two pathways for  $\text{CO}_3^{2-}$  adsorption. (c) The  $\text{CO}_3^{2-}$  adsorption energy ( $E_{\text{ads}}$ ) in lattice O surface and O defects surface by two pathways. (d)  $\text{C}_2\text{H}_6$  adsorption energy ( $E_{\text{ads}}$ ) in  $\text{NaCo}_2\text{O}_4$  (100) surface.



lattice O of CeO<sub>2</sub> could also exist CO<sub>3</sub><sup>2-</sup> OR. From all these results, in the overall CO<sub>3</sub><sup>2-</sup> OR on 2NaCo<sub>2</sub>O<sub>4</sub>/CeO<sub>2</sub> surface, CeO<sub>2</sub> could indeed separate a portion since C<sub>2</sub>H<sub>6</sub> OR could happen on NaCo<sub>2</sub>O<sub>4</sub>.

The adsorption energy of C<sub>2</sub>H<sub>6</sub> on NaCo<sub>2</sub>O<sub>4</sub> was calculated to investigate the competition of CO<sub>3</sub><sup>2-</sup> OR and C<sub>2</sub>H<sub>6</sub> OR. From Fig. 5d, the E<sub>ads</sub> on lattice O is −0.056 eV, which is lower than that of O defects (−0.041 eV). Comparing with the E<sub>ads</sub> of CO<sub>3</sub><sup>2-</sup> OR, the number had a significant decline, which demonstrates that C<sub>2</sub>H<sub>6</sub> OR is unfavorable. This proves that the CO<sub>3</sub><sup>2-</sup> OR has a great effect on reducing the reaction energy barrier of C<sub>2</sub>H<sub>6</sub>.

#### 4. Conclusion

We explored the incomplete oxidation of alkanes and chose ethane to be reactant as a example. In this process, we found a relationship between the electrolyte and target reactants and offered a solution to control this two reaction. In this study, the NaCo<sub>2</sub>O<sub>4</sub> has a strong capability of both CO<sub>3</sub><sup>2-</sup> OR and C<sub>2</sub>H<sub>6</sub>OR, to regulate these two reactions, CeO<sub>2</sub> was composited with NaCo<sub>2</sub>O<sub>4</sub> to decline C<sub>2</sub>H<sub>6</sub> OR. We found the best ratio of these two catalysts and converted C<sub>2</sub>H<sub>6</sub> to 2-propanol and acetone. Furthermore, the changing process of catalysts was recorded and we found that the lattice O had a great increase and the O defects were declined. After comparing the capability of CO<sub>3</sub><sup>2-</sup> OR and C<sub>2</sub>H<sub>6</sub> OR, we confirmed that lattice O on NaCo<sub>2</sub>O<sub>4</sub> was the active site for C<sub>2</sub>H<sub>6</sub> OR and CO<sub>3</sub><sup>2-</sup> OR mainly occurred on O defects. In addition, the relationship of these two reactions was inferred that the CO<sub>3</sub><sup>2-</sup> OR could promote the C<sub>2</sub>H<sub>6</sub> OR and must exist, however, excessive CO<sub>3</sub><sup>2-</sup> OR could restrain the C<sub>2</sub>H<sub>6</sub> OR. Moreover, the reaction pathway of C<sub>2</sub>H<sub>6</sub> OR was inferred by in situ ATR-FTIR and the conclusions obtained before. DFT calculation was also verified these conclusion and speculated the mechanism of how CO<sub>3</sub><sup>2-</sup> promote the target reaction. In conclusion, improving the performance of catalysts is not the best way in this competitive system, regulating the different reactions and find the balance is the key factor to achieve target reaction.

#### Funding Information

This work was supported by National Natural Science Foundation of China (U20A20130), Hebei Natural Science Foundation (B2021208033, B2022208040).

#### CRediT authorship contribution statement

**Jiaqi Lv:** Methodology, Formal analysis. **Xuan Liu:** Investigation, Formal analysis. **Xuerui Hao:** Methodology, Formal analysis. **Erhong Duan:** Writing – review & editing, Supervision, Resources, Funding acquisition. **Yubo Zhang:** Writing – original draft, Investigation, Formal analysis, Data curation. **Saifei Wang:** Writing – review & editing, Funding acquisition, Formal analysis.

#### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

#### Data availability

No data was used for the research described in the article.

#### Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.apcatb.2024.124063.

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